ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF ALKYLATED LINEAR AMINE LIGANDS AND THEIR OPTIMIZATION FOR ATOM TRANSFER RADICAL POLIMERIZATION

M.Sc. Thesis by
Çağlar Remzi BECER

Department : Polymer Science and Technology

Programme: Polymer Science and Technology

JUNE 2005

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LİNEER AMİN LİGANDLARIN SENTEZİ VE ATOM TRANSFER RADİKAL POLİMERİZASYONU İÇİN OPTİMİZASYONU

YÜKSEK LİSANS TEZİ

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LIST OF SYMBOLS

$\mathbf{M_n}$	**:** Number average molecular weight of polymers
$\mathbf{M_w}$	**:** Weight average molecular weght of polymers
$\mathbf{M_n / M_w}$	**:** Molecular weight distribution of polymers
PMMA	**:** Polymethyl methacrylate
$\mathbf{k_{act}}$, $\mathbf{k_{deact}}$	**:** Rate constants of activation and deactivation steps of the initiation in radical polymerization
$\mathbf{K_{eq}}$, $\mathbf{k_p}$	**:** Equilibrium rate constant and rate constant of propagation step in radical polymerization respectively
$\mathbf{k_t}$	**:** Rate constant of termination
I, M	**:** Initiator and monomer respectively

SYNTHESIS OF ALKYLATED LINEAR AMINE LIGANDS AND THEIR OPTIMIZATION FOR ATOM TRANSFER RADICAL POLIMERIZATION

SUMMARY

Atom transfer radical polymerization (ATRP) is one of the most successful system in controlled radical polymerization. Transition metal catalysts are the key to ATRP since they determine the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The main effect of the ligand is to solubilize the transition-metal salt in organic media and to regulate the proper reactivity and dynamic halogen exchange between the metal center and the dormant species or persistent radical.

In this study, novel ligands synthesized with Hoffmann reaction of N,N-bis(2-aminoethyl)amine, N-{2-[(2-aminoethyl)amino]ethyl}ethane-1,2-diamine and poly(ethylene imine) with linear alkylbromides which have different chain lengths (R-: C2H5-, C3H7-, C4H9-, C5H11-, C6H13-). The homogenity obtained in controlled living polymerization media due to these ligands provides well-defined polymeric structures with low polydispersity.

ALKİLLENMİŞ LİNEER AMİN LİGANDLARIN SENTEZLENMESİ VE ATOM TRANSFER RADİKAL POLİMERİZASYONU İÇİN OPTİMİZASYONU

ÖZET

Atom Transfer Radikal Polimerizasyonu, kontrollü radikal polimerizasyon sistemleri içerisinde en başarılı olan sistemlerden biridir. Geçiş metali katalizleri, pasif ve aktif parçacıklar arasındaki atom transfer dengesi ile değişim dinamiğini belirlediği için ATRP'nin en önemli bileşenlerindendir. Ligandın ana etkisi, geçiş metalini organik ortamda çözünür hale getirmek ve pasif ve aktif veya mevcut radikal arasında dinamik halojen değişimini ve uygun reaktiviteyi düzenlemektir.

Bu çalışmada, değişik zincir uzunluklarındaki (R-: C2H5-, C3H7-, C4H9-, C5H11-, C6H13-) lineer alkilbromürlerin N,N-bis(2-aminoetil)amin, N-{2-[(2-aminoetil)amino]etil}etan-1,2-diamin ve poli(etilenimin)'nin Hoffmann reaksiyonu ile yeni ligandlar sentezlenmiştir. Bu ligandlar ile kontrollü yaşayan polimerizasyon ortamında homojenlik sağlanmış ve ayrıca düşük molekül ağırlığı dağılımı ile iyi tanımlanmış polimerik yapılar elde edilmiştir.

1. INTRODUCTION

Metal-mediated radical polymerization, more generally known as atom transfer radical polymerization (ATRP) has become one of the most efficient and widely used controlled radical polymerization method to obtain polymers and copolymers with different topologies.

Transition metal catalysts are the key to ATRP since they determine the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The main effect of the ligand is to solubilize the transition-metal salt in organic media and to regulate the proper reactivity and dynamic halogen exchange between the metal center and the dormant species or persistent radical. Ligands, typically amines or phosphines, are used to increase the solubility of the complex transition metal salts in the solution and to tune the reactivity of the metal towards halogen abstraction. So far, a range of multidentate neutral nitrogen ligands was developed as active and efficient complexing agents for copper-mediated ATRP. Tridentate and tetradentate aliphatic amines ligands generally provide faster polymerizations than bidentate ligands, while monodentate nitrogen ligands yield redox-initiated free radical polymerization. In addition, ligands with an ethylene linkage between the nitrogens are more efficient than those with a propylene or butylene linkage.

Linear amines with ethylene linkage like tetramethylethylenediamine (TMEDA), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) were synthesized and examined for ATRP as ligands. Reasons for examining of these type of ligands are, they have low price, due to the absence of the extensive π-bonding in the simple amines, the subsequent copper complexes are less colored and since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-bpy complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates.

Solubility of the ligand and its metal complexes in organic media is of particular importance to attain homogeneous polymerization conditions. The rate of polymerization is also affected by the relative solubilities of the activating and the deactivating species of the catalyst. In heterogeneous systems, a low stationary concentration of the catalyst species allows for a controlled polymerization, but the polymerization is much slower than in homogeneous systems. The ligand with a long aliphatic chain on the nitrogen atoms provides solubility of its metal complexes in organic solvents. However, the increasing length of the alkyl substituents induces steric effects and can alter the redox potential of the metal center. Any shift in the redox potential affects the electron transfer and the activation-deactivation equilibrium.

In this thesis, in order to demonstrate effect of homogeneity, a series of ligands with reaction of diethylenetriamine, triethylenetetramine and poly(ethylene imine) with linear alkylbromides which have different chain lengths (C2H5-, C3H7-, C4H9-, C5H9-, C6H13-) were synthesized, according to the literature [1]. Linear amine ligands were selected because of low price, robust and versatile synthesizing conditions. After synthesizing, alkylated tri, tetra and multidentate nitrogen ligands were used in optimization of ATRP conditions for both methyl methacrylate (MMA) and styrene (S), which were carried out in the presence of CuBr as co-catalyst with suitable initiators. The well-defined polymers with low polydispersities were obtained due to the homogeneity of the polymerization facilitated by these ligands.

2. THEORETICAL PART

2.1. Controlled/Living Radical Polymerizations

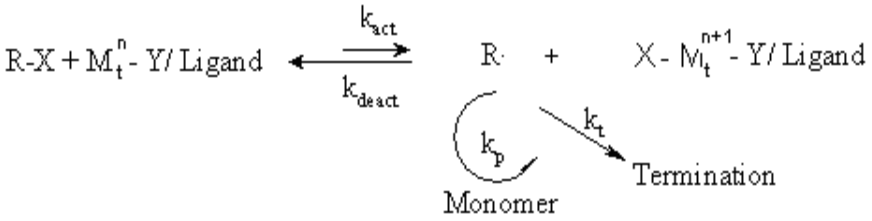
The development of controlled/living radical polymerization (CRP) methods has been a long-standing goal in polymer chemistry, as a radical process is more tolerant of functional groups and impurities and is the leading industrial method to produce polymers [2]. The advent of controlled/living radical polymerization (CRP) enables preparation of many new materials such as well defined components of coatings (with narrow MWD, precisely controlled functionalities), non ionic surfactants, polar thermoplastic elastomers, entirely water soluble block copolymers (agents for crystal engineering), gels and hydrogels, lubricants and additives, surface modifiers, hybrids with natural and inorganic polymers, various biomaterials and electronic materials. This is very important since free radical polymerization is the most common method of making polymeric materials [3].

The controlled/living systems, are quite similar to the conventional ones, however, the radical formation is reversible. Similar values for the equilibrium constants during initiation and propagation ensure that the initiator is consumed at the early stages of the polymerization, generating chains, which slowly and continuously grow, like in a living process [4]. Currently three systems seem to be most efficient: Nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and degenerative transfer processes such as RAFT [5]. Each of the CRPs has some limitations and some special advantages and it is expected that each technique may find special areas where it would be best synthetically suited. For example, NMP carried out in the presence of bulky nitroxides cannot be applied to the polymerization of methacrylates due to fast β-H abstraction. ATRP cannot yet be used for the polymerization of the acidic monomers, which can protonate the ligands and complex with copper. RAFT is very slow for the synthesis of low molecular weight polymers due to trapping of growing radicals by the intermediate radicals. At the same time each technique has some special advantages. Terminal alkoxyamines

may act as additional stabilizers for some polymers. Atom transfer radical polymerization enables the synthesis of special block copolymers by utilizing a halogen exchange and has an inexpensive halogen at the chain end [6]. RAFT can be applied to the polymerization of many unreactive monomers, such as vinyl acetate [7].

2.2. Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well-defined low molecular weight polymers [8]. A general mechanism for ATRP is given below.



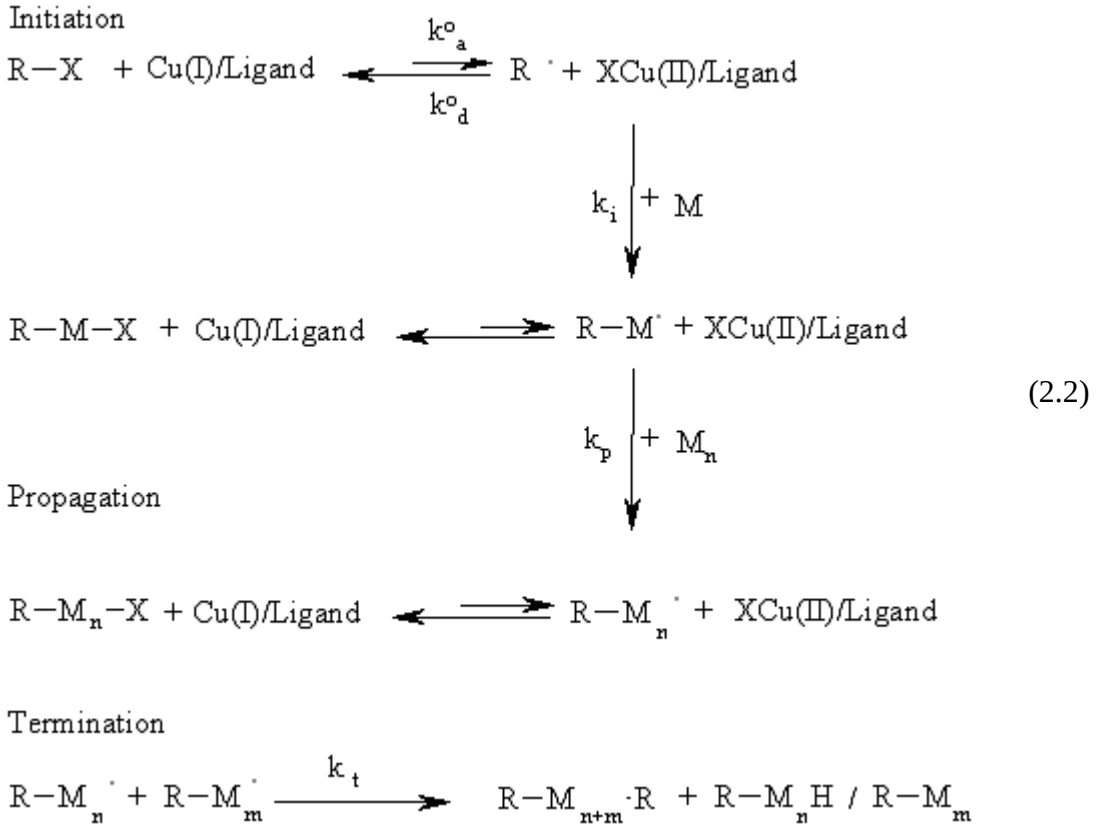
(2.1)

ATRP is based on the reversible transfer of an atom or group from a dormant polymer chain (R-X) to a transition metal (M_t^n / Ligand) to form a radical (R•), which can initiate the polymerization, and a metal-halide whose oxidation state has increased by one (X-M_t^{n+1} / Ligand); the transferred atom or group is covalently bound to the transition metal. A catalytic system employing copper (I) halides (M_t^n / Ligand) complexed with substituted 2,2'-bipyridines (bpy) has proven to be quite robust, successfully polymerizing styrenes, various (meth)acrylates, acrylonitrile and other monomers [9-10].

This process occurs with a rate constant of activation, k_{act}, and deactivation, k_{deact}. Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination.

Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the

initial, short, nonstationary stage of polymerization. This process generates oxidized metal complexes, $X\text{-}M_t^{n+1}$, as persistent radicals to reduce the stationary concentration of termination [11]. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_{deact}, and also with the concentration of deactivator [4]. The molecular conversion and the amount of initiator used, $DP=\Delta[M]/[I]_0$; polydispersities are low, $M_w / M_n < 1{,}3$ [12].



(2.2)

The ATRP system is consisting of the monomer, initiator, and catalyst composed of transition metal species with any suitable ligand.

2.2.1. Monomers

A variety of monomers have been successfully polymerized using ATRP. Typical monomers include styrenes, (meth)acrylates, (meth)acrylamides, dienes, acrylonitrile, and other monomers which contain substituents that can stabilize the propagating radicals. Even under same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination

by coupling or disproportionation, the magnitude of the equilibrium constant determines ($k_{eq} = k_{act}/k_{deact}$) the polymerization rate. ATRP will not occur very slowly if the equilibrium constant is too small. In contrast, too large and equilibrium constant will lead to a large amount of termination because of high radical concentration [13].

2.2.2. Initiators

The amount of the initiator in the ATRP determines the final molecular weight of the polymer at full monomer conversion. Multifunctional initiators may provide chain growth in several directions. The main role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator in a living polymerization.

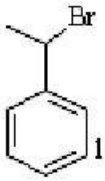
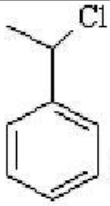
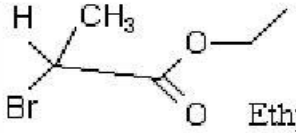
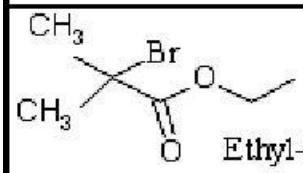
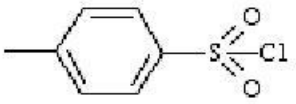
$$\mathbf{DP = [M]_0 / [I]_0 \times Conversion} \qquad (2.3)$$

In ATRP, alkyl halides (RX) are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group X, must rapidly and selectively migrate between the growing chain and the transition-metal complex.

Initiation should be fast and quantitative with a good initiator. In general haloganated alkanes, benzylic halides, α-haloesters, α-haloketones, α-halonitriles and sulfonyl halides are used as ATRP initiators [13].

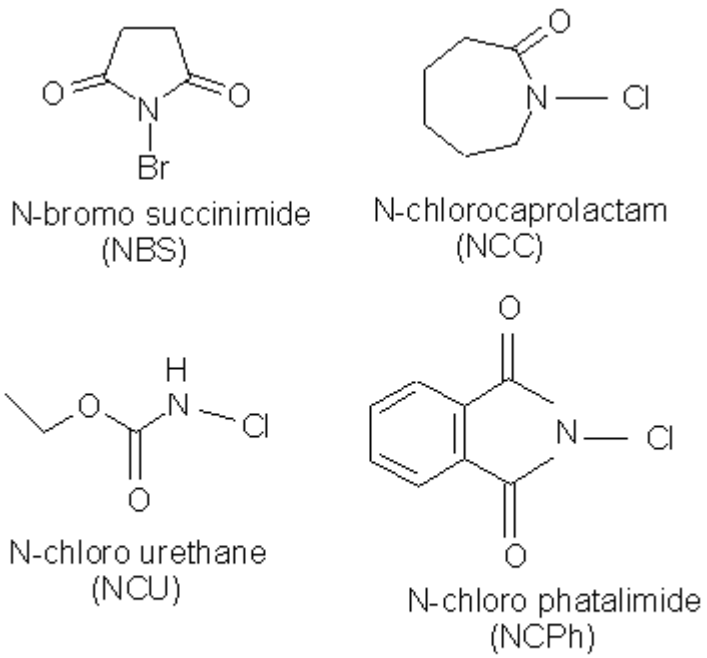
The most frequently used initiator types used in the atom transfer radical polymerization systems are given in Table 2.1.

Table 2.1. Types of initiators used in ATRP systems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo propionate	Methyl methacrylate and Styrene
 Ethyl-2-bromo isobutyrate	Methyl methacrylate and Styrene
 p-toluene sulphonyl chloride	Methylmethacrylate

Two parameters are important for a successful ATRP initiating system; first, initiation should be fast in comparison with propagation. Second, the probability of side reactions should be minimized [13].

The only class of initiators that provide much higher rate of initiation than propagation with methacrylates, styrenes, acrylates and acrylonitrile is based on functional alkyl and aryl sulfonyl chlorides [14,15]. The N-centered radical chemistry is not well understood except for some classic reactions such as Hoffmann-Lofller [16,17] or benzylic (allylic) halogenations [18]. Some of the N-halogenated derivatives used as initiators for the living radical polymerization of ethyl methacrylate are given in below.



(2.4)

2.2.3. Transition metal complexes

Catalyst is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prequisities for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a halogen. Fourth, the ligand should complex the metal relatively strong. The most important catalysts used for ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3/Al(OiPr)_3$.

2.2.4. Ligands

The main role of the ligand in ATRP is to solubilize the transition-metal salt in the organic media and adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer [19]. They control the selectivity by

steric/electronic effects. The effect of ligands on Atom Transfer Radical Polymerization will be discussed widely in Section 2.3.

2.2.5. Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system. Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethylacetate, acetone, dimethylformamide (DMF), ethylene carbonate, alcohol, water, carbondioxide, and some others, are being used for different kinds of monomers. A solvent is sometimes necessary when the obtained polymer is insoluble in its monomer. Chain transfer to solvent should be minimum.

2.2.6. Temperature and reaction time

The rate of polymerization also determines the rate of polymerization by effecting both propagation rate constant and the atom transfer equilibrium constant. The k_p/k_t ratio increase as a result of higher temperature thus enables us better control over the polymerization. However this may also increase the side reactions and chain transfer reactions. The increasing temperature also increases the solubility of the catalyst. Against this, it may also poison catalyst by decomposition. Determining the optimum temperature; monomer, catalyst and the targeted molecular weight should be taken into consideration.

2.2.7. Molecular weight and molecular weight distribution

We can determine the average molecular weight of the polymer by the ratio of consumed monomer and the initiator as in a typical living polymerization ($DP_n=\Delta[M]/[I]_o$, DP=degree of polymerization) while there is a narrow molecular weight distribution ($1.0 < Mw/Mn < 1.5$).

The molecular weight distribution or polydispersity Mw / Mn is the index of the polymer chain distribution. In a well-controlled polymerization, Mw / Mn is usually less than 1.1. The polydispersity index in ATRP in the absence of chain termination and transfer is shown below.

$$\mathbf{M_w / M_n = 1 + [[RX]_o k_p / k_d [D]] . [(2/p) - 1]} \qquad (2.5)$$

Where, D: Deactivator, k_p: Propagation rate constant, k_d: Deactivation rate constant, p: Monomer conversion

When a hundred percent of conversion is reached, in other words p=1, it can be concluded that;

i) Polydispersities (molecular weigh distributions) decrease, if the catalyst deactivates the chains faster (smaller k_p / k_d)

ii) For the smaller polymer chains, higher polydispersities are expected to obtain because the smaller chains include little activation-deactivation steps resulting in little control of the polymerization.

iii) Polydispersities decrease as the concentration of the deactivator decreases. (For example, the addition of a small amount of Cu(II) halides in copper-based ATRP decreases the reaction rate thus leads to better controlled polymerizations)

2.2.8. Kinetic of ATRP

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction usually negative first order with respect to the deactivator (CuX_2 / Ligand). The rate equation of ATRP is formulated in discussed conditions and given below.

$$R_p = k_{app}[M] = k_p[P\cdot][M] = k_p K_{eq}[I]_0 \frac{[Cu(I)]}{[Cu(II)X]}[M] \qquad (2.6)$$

Results from kinetic studies of ATRP for styrene, methyl acrylate (MA), and methyl methacrylate (MMA) under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator, and Cu(I) complex concentrations.

If the deactivation does not occur, if it is too slow ($k_p >> k_d$), there will be no difference between ATRP and the classical redox reactions and the termination and transfer reactions may be observed. To gain better control over the polymerization,

addition of one or a few monomers to the growing chain in each activation step is desirable.

2.3. The Effect of ligands on ATRP

Controlled/ living radical polymerization has been a field of intensive research in recent years. Several new methodologies have been developed to gain better control over molecular weight, molecular weight distribution, and architectures of polymers [20]. Transition metal catalyzed atom transfer radical polymerization (ATRP) is one of the most successful systems [21]. The basic concept of ATRP is based on atom transfer radical addition reaction (ATRA) in organic chemistry, which is sometimes referred to as Kharasch addition. In a typical ATRP system, alkyl halides are used as the initiators, transition metals with multiple accessible oxidation states are used as the catalysts, and ligands, typically amines or phosphines, are used to increase the solubility of the transition metal salts in solution and to tune the reactivity of the metal towards halogen abstraction. The polymerization involves the activation of the dormant species, Pn-X, through halogen abstraction by the transition metal in its lower oxidation state, M_t^n, to form propagating species, carbon-centered radical P•, and the transition metal in its higher oxidation state, X-M_t^n. The radical can add to alkene to form a new carbon-centered radical, PM•, or it can be deactivated through halogen transfer from the transition metal in its higher oxidation state to form dormant alkyl halide, PMX. If PMX can be reactivated by halogen abstraction, the alkene addition and halogen transfer reactions are repeated, and a polymer is obtained. Of course, more than one monomer unit can be incorporated in one activation step.

The key to the control in ATRP is the dynamic equilibrium between the active species (propagating radical) and dormant species (alkyl halide) via halogen transfer. Several factors are important in order to achieve good polymerization control. First, fast and quantitative initiation ensures that all polymer chains start to grow at about the same time. When the contribution from chain termination and transfer reactions is significantly small, the degree of the polymerization (DP_n) can be predetermined by the ratio of consumed monomer and the initiator ($DP_n = \Delta[M]/[I]_0$). Second, the equilibrium between the alkyl halide and transition metal is strongly shifted to the

dormant species. This equilibrium position will render most of growing polymer chains stored in the dormant species reservoir and a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third, fast deactivation of propagating radicals by halogen transfer assures that all polymers chains-are growing at approximately the same rate leading to narrow molecular weight distributions. Fourth, a relatively fast activation of dormant polymer chains gives rise to a reasonable polymerization rate. Fifth, there should be no side reactions such as β-H abstraction or reduction/oxidation of radicals. Originally, two ATRP systems were imported in 1995. Sawamoto et al. reported the controlled polymerization of methyl methacrylate (MMA) with $Ru(PPh_3)_3Br_2$ as the catalyst in conjunction with aluminum alkoxide as the activator [22]. Matyjaszewski et al. reported the controlled polymerizations of styrene and (meth)acrylates using CuX (X = Cl, Br) complexed by 2,2'-bipyridine (bpy) as the catalyst [23,24]. Since then, many new catalytic systems employing other transition metals, such as Ni [25,26] and Fe [27,28] have been reported. Copper system is one of the most extensively studied and also one of the most promising in terms of cost and versatility. It has been applied toward the preparation of a large variety of well-defined polymers such as styrenics, (meth)acrylic esters, and acrylonitrile [29]. This brief overview describes the recent development in new catalytic systems in the copper-mediated ATRP, focusing on the design, synthesis and application of new nitrogen ligands.

One of the challenges in ATRP is to extend the scope of monomers that can be polymerized in a controlled manner. This can be accomplished through the development of more active catalysts. For a specific metal, catalytic activity is varied by the employment of different ligands. Thus, detailed studies of the effect of ligands can provide more insightful information in catalyst design.

Transition metal catalysts are the key to ATRP since they determine the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several basic prerequisites for the transition metal. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second, the metal center should have reasonable affinity towards

halogen. Third, the metal coordination sphere should be expandable upon oxidation to selectively accommodate a (pseudo)halogen.

The role of the ligand in ATRP is to solubilize the transition metal salts in organic media and to adjust the metal center for an appropriate reactivity and dynamics in halogen exchange. The electron donating ability of the ligand can greatly affect the redox potential of the transition metal complex and influence the reactivity of the metal center in halogen abstraction and transfer. In general, transition metal catalysts with low redox potentials favor the formation of copper(II) species and are active catalysts in ATRP with fast polymerization rate. In contrast, transition metal catalysts with high redox potentials disfavor the formation of copper(II) species and are not reactive in halogen abstraction. These transition metal catalysts tend to lead to slow or not well-controlled polymerization. However, even in the most thoroughly studied copper/bpy catalytic system, the exact structure of the active species is not completely clear. The literature data on the coordination chemistry of copper species in non-polar solvents are limited. In addition, both copper(I) and copper(II) species are quite labile in solution which renders structural studies difficult. Preliminary EPR and UV-Vis studies suggested the presence of quite complex species in polymerization solution. ^{1}H NMR studies indicate copper(l) coordinated by bpy is in fast exchange with the free ligand in solution. Combined with the literature data on the structure of copper/bpy complex in polar solvents, such as methanol and acetonitrile, it can be assumed that during ATRP the majority of the copper species can be best represented by a tetrahedral Cu(I)/$(bpy)_2$ [30] and a trigonal bipyramidal XCu(II)/$(bpy)_2$ (Figure 2.1) [31]. Other transition metal complexes with only halides as the ligands or bridged structures are also possible.

The effectiveness of the catalyst is greatly influenced by the choice of ligand. Nitrogen ligands generally work well for copper-mediated ATRP. In contrast, sulfur, oxygen or phosphorous ligands are less effective due to the inappropriate electronic effects or unfavorable binding constants. Many monodentate nitrogen ligands can provide coordination for copper; however, the resulting copper complexes do not promote successful ATRP.

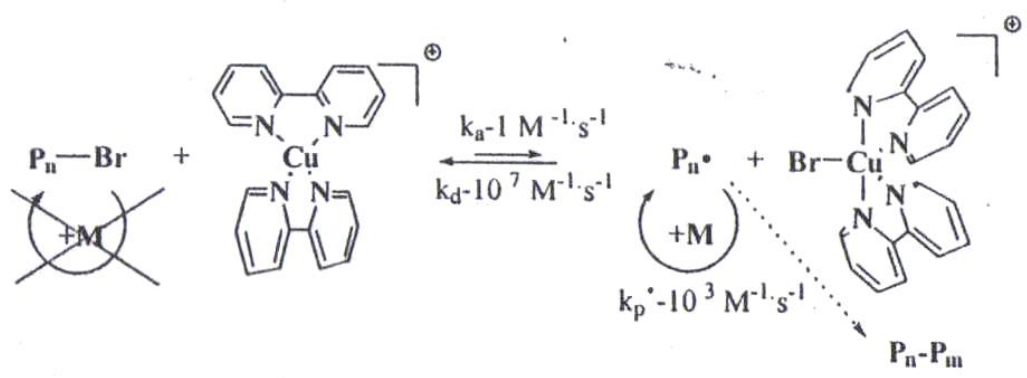


Figure 2.1 Proposed copper(I) and copper (II) species using bpy as the ligand

The nitrogen donors in multidentate ligands can be classified in several different ways. 1. According to the electronic property of the coordinating nitrogen atom, ligands can be separated into those with aromatic nitrogen, aliphatic nitrogen, imine nitrogen, and mixed nitrogen ligands. 2. According to geometry, ligands can be separated into linear, cyclic and branched (e.g., tripodal) structures. 3. According to the coordination number, ligands can be separated into monodentate, bidentate, tridentate, tetradentate ligands, etc. The coordination number of the nitrogen ligand plays the most important role in determining the control and rate of the polymerization (vide infra). Thus, ligands can be discussed in the following three major categories: bidentate, tridentate and tetradentate nitrogen ligands. In most cases, the polymerization conditions were kept the same or similar to facilitate comparison; however, be cautioned not to place too much emphasis on comparing the rates of the polymerizations as these are all apparent and are affected by many intrinsic factors, such as copper(I) and copper(II) concentrations in the solution and the rate of deactivation of the growing radicals.

2.3.1. Bidentate nitrogen ligands

Bidentate nitrogen ligands are readily available and have been most systematically studied for copper-mediated ATRP. X-ray structures have been solved for some of the copper-ligand complexes. In general, complexes of copper(I) and bidentate ligands exhibit a distorted tetrahedral arrangement of two coordinating ligands surrounding the metal center. Kinetic studies of the homogeneous polymerizations of both styrene and MA suggest a 2/1 ratio of ligand to metal is needed to achieve

maximum rate of polymerization [32,33]; however, a 1/1 ratio is enough for MMA under homogeneous conditions [34]. According to their electronic properties, bidentate ligands are discussed in the following subgroups: bipyridine ligands, diamine ligands, diimine ligands, and mixed ligands.

2.3.1.1. Bipyridine derivatives

Bpy was the first ligand used to successfully promote copper-mediated ATRP of styrene and (meth)acrylates [33,34] Linear semilogarithmic kinetic plots and linear increase of molecular weights with monomer conversion have been observed. The experimental molecular weights were close to the theoretical values as predicted by the following equation: $M_{n,Cal} = ([M]_o/[In]_o)$ x $(MW)_o$ x conversion, where $[M]_o$ and $[In]_o$ represent the initial concentrations of monomer and initiator, and $(MW)_o$ is the molecular weight of the monomer. Polydispersities were quite narrow (M_w/M_n ~ 1.2 - 1.5). These results suggest that initiator efficiency was high, and the number of chains was approximately constant, which was consistent with the criteria for a controlled polymerization. However, the $CuX(bpy)_2$ catalytic system is heterogeneous in non-polar media which rendered further kinetic studies difficult. Reverse ATRP, which employs a conventional radical initiator such as azobisisobutyronitrile (AIBN) in the presence of copper(ll) species to promote a controlled polymerization; was difficult with bpy as the ligand due to the low solubility of copper(II) species [35]. A large excess of bpy was used in an attempt to increase the solubility of copper(II) in the polymerization and the control of the polymerization was unsuccessful for (meth)acrylates under the reaction conditions.

4,4'-Di-n-heptyl-2,2'-bipyridine (dHbpy), 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy) and 4,4'-di-n-nonyl-2,2'-bipyridine (bpy9) were synthesized to provide homogeneous copper complexes in ATRP (Figure 2.2.) [36,37]. Polymers with very low polydispersities (M_w/M_n~1.05) were prepared using the homogeneous catalysts (17). This was attributed to the increased rate of deactivation of the growing radicals in solution. Kinetic studies were possible for these systems [32-34]. Reverse ATRP with AIBN as the initiator have been successfully carried out under homogeneous conditions for the polymerizations of styrene, MA and MMA [38]. When

perfluoroalkyl side chains were attached to bpy (dR6*f*bpy, Figure 2.2), controlled polymerizations were performed in supercritical carbon dioxide [39].

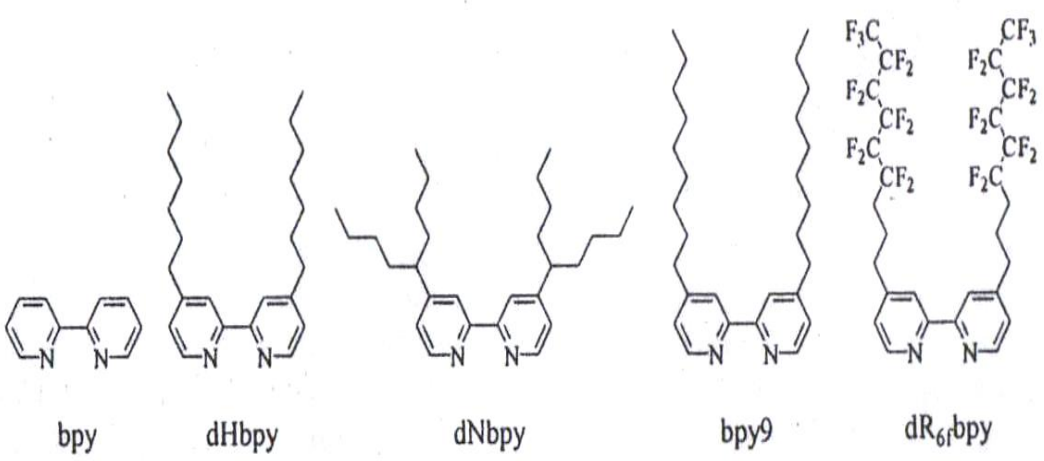


Figure 2.2 Structures of some bpy derivatives

Electron-donating groups on bpy can form copper complexes with lower redox potentials which shift the equilibrium more towards radical formation, mid hence lend to a faster polymerization rate. In contrast, electron-withdrawing groups on bpy provide copper complexes with higher redox potentials, which shift the equilibrium to the dormant species. For example, copper(I) complexed by 4,4'-dicarboxylate-2,2'-bipyridine was so stable that it was difficult to abstract halide from alkyl halide or polymeric halide to form radicals. Steric effect is another important consideration in ligand design. Substitutions on the 6,6' positions of bpy leads to uncontrolled polymerization, largely due to the unfavorable steric effect for the formation of copper(II) species since it becomes more difficult for copper(II) to accept incoming halogens and to adopt the sterically more demanding triagonal bipyramidal configuration [41] Similar result has been previously reported [37].

1,10-Phenanthroline and its derivatives have also been used successfully as the ligands for copper-mediated ATRP of styrene [40]. Solubilities of the copper complexes were found to be an important factor in controlling the polymerization. The lowest polydispersities were obtained under homogeneous conditions using 4,7-diphenyl-l,10-phenanthroline as the ligand and 1,2-dimethoxybenzene as the solvent.

2.3.1.2. Diamine ligands

The most common diamine ligand is ethylenediamine (EDA) and its derivatives. They are inexpensive and readily available. Generally, copper complexes coordinated by unalkylated ligands have low solubilities in common organic solvents and lead to ill-controlled polymerizations. Alkylation of EDA greatly improves its ability to solubilize transition metals in organic solvents. Sterics plays a significant role in the catalytic activities of alkylated ethylenediamines. Compared to bpy, N,N,N',N'-tetramethylethylenediamine (TMEDA) leads to relatively controlled polymerizations of styrene, MA and MMA with relatively high polydispersities (M_w/M_n~1.4) and low rates of polymerization [41]. Computer modeling illustrates the significant steric hindrance between the methyl groups on nitrogen upon halogen abstraction by the copper(I)/$(TMEDA)_2$ complex. When the sterics on the nitrogen atoms was increased further, as in the case of 2-(dimethylamino)ethyl morpholine or tetraethylethylenediamine, ill-controlled polymerizations were observed yielding polymers with much higher molecular weights than the predicted values and high polydispersities It has to be recognized that ATRP equilibrium constants and propagation rate constants of styrene, MA and MMA are quite different. For example, the values of equilibrium constant using CuBr/$(dNbpy)_2$ as the catalyst are approximately $K_{eq} \sim 4x10^{-8}$ (styrene at 110 °C), $K_{eq} \sim 1.2x10^{-9}$ (MA at 90 °C), and $K_{eq} \sim 7x10^{-7}$ (MMA at 90 °C). Under the same conditions, the values of rate constant are $k_p \sim 1.6xl0^3$ $M^{-1}S^{-1}$ (styrene), $k_p \sim 5.0xl0^4$ $M^{-1}S^{-1}$ (MA), and $k_p \sim 1.0x10^3$ $M^{-1}S^{-1}$ (MMA). Thus, in order to have a reasonable polymerization rate (e.g., 50% monomer conversion in ca. 3 h), it is necessary to adjust concentrations, temperature and dilution. The following conditions were typically used for the three standard monomers: styrene: bulk, 110 °C, $[styrene]_o/[initiator]_o/[catalyst]_o$ = 96/1/1; MA: bulk; 90 °C; $[MA]_o/[initiator]_o/[catalyst]_o$ = 232/1/1; MMA: 50 vol % anisole; 90°C; $[MMA]_o/[initiator]_o/[catalyst]_o$ = 200/1/1. In addition, initiators resembling dormant species were used. PEBr (PEBr = 1-phenylethyl bromide or (l-bromoethyl)benzene), EBP (EBP = ethyl 2-bromopropionate) and EB*i*B (EB*i*B = ethyl 2-bromoisobutyrate) were used for styrene, MA and MMA, respectively. Effect of the spacer length between the nitrogen ligands was also studied by research groups using TMEDA, N,N,N',N'-tetramethyl-propylenediamine (TMPDA) and N,N,N',N'-tetramethylbutylenediamine (TMBDA). Increase of the number of carbons between

the two nitrogen, the control of the polymerization progressively degraded with higher molecular weight polymers formed at very low monomer conversions. In the case of TMBDA, the polymerizations displayed behavior typical for redox-initiated free radical polymerization.

2.3.1.3. Diimine ligands

Diimines usually do not function well as ligands in copper-mediated ATRP due to the high steric hindrance [42,43]. For example, polymerizations employing N,N'-di-(2,4,6)-trimethylphenyl ethylenediimine as the ligand yielded polymers with much higher molecular weights than theoretical values [42].

2.3.1.4. Bidentate ligands with mixed nitrogen types

Pyridine-imine mixed nitrogen ligands have been prepared and successfully used for the ATRP of MMA [43-45]. The ligands can be easily prepared by the condensation reactions between the appropriate aldehyde, or ketone, with a primary amine. In one paper, several N-alkyl-(2-pyridyl)methanimine, where alkyl = *n*-butyl (*n*BPMI), isobutyl (*i*BPMI), *sec*-butyl (*s*BPMI), *n*-propyl (*n*PPMI), and N-(*n*-propyl)-l-(2-pyridyl)ethanimine (PPEI) were synthesized and used in ATRP (Figure 2.3) [45]. In all cases, the experimental molecular weights increased linearly with conversion and were slightly higher than the theoretical values. Polydispersities remained low for polymers produced using copper complexed by *n*BPMI, *s*BPMI and *n*PPMI (M_w/M_n ~ 1.3); however, polydispersities were relatively high for polymers produced using copper complexed by *s*BPMI and *n*PPEI (M_w/M_n > 1.5). Polymerizations using *n*BPMI, *n*PPMI and *n*PPEI are significantly faster than those using *i*BPMI and *s*BPMI. In general, it was concluded that catalysts, which contain n-alkyl substituents, are more effective than those containing branched alkyl substituents in the imine group. The cause of these effects is not well understood and is presumed to be related to the steric and electronic effect upon oxidation of copper(I).

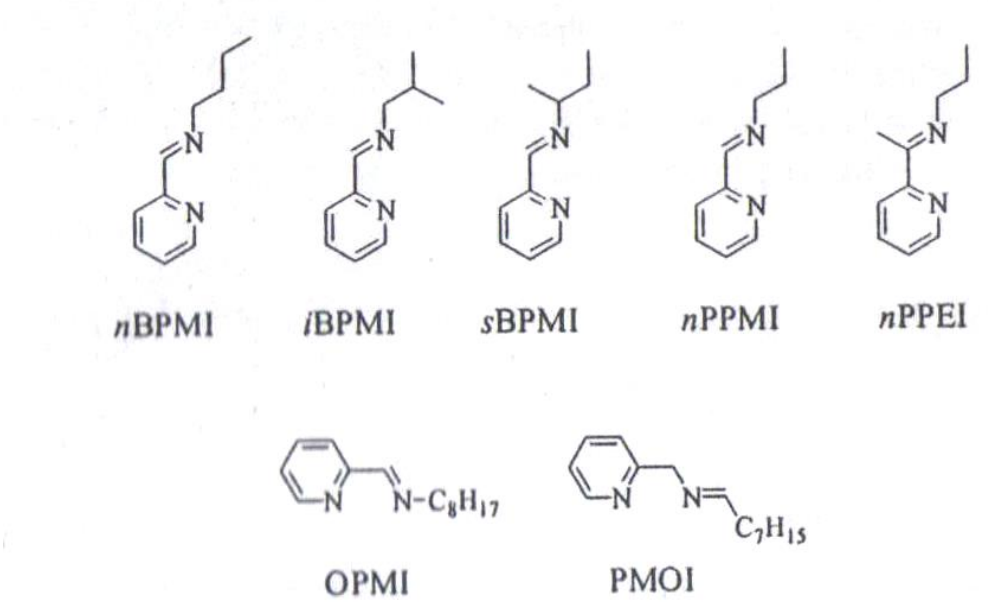


Figure 2.3 Structures of pyridine-imines

Other unconjugated pyridine-imine type ligands, such as N-(2-pyridylmethyl)-l-octanimine (PMOI), have also been studied [46]. Compared with its conjugated analog, N-(*n*-octyl)-(2-pyridyl)methanimine (OPMI), PMOI led to significantly faster polymerizations. Both ligands provided reasonably controlled polymerizations where the experimental molecular weights were close to the theoretical values with relatively low polydispersities. The difference in the rate of polymerization can partially be ascribed to the different electronic properties of the ligands. The LUMO π^* orbital in the conjugated π system in the case of OPMI provides lower lying empty orbitals for delocalizing the electron density away from the transition metal center than PMOI and thus better stabilizes the metal center in its low oxidation state. As a result, the copper(I)/copper(II) redox potential is increased which can lead to a slower polymerization.

2.3.2. Tridentate nitrogen ligands

Tridentate nitrogen ligands are fairly common and have found many applications in various areas of organometallic chemistry. With the increase in coordination number, larger varieties of ligands are possible by different combinations of nitrogen types and geometries. In contrast to bidentate ligands, which form cationic tetrahedral complexes, tridentate ligands form 1:1 uncharged complexes with copper. As a result, one equivalent of the tridentate ligand (to metal) is sufficient to achieve

maximum polymerization rate. According to the type of nitrogens, the tridentate nitrogen ligands are discussed in the following subgroups: tripyridine ligands, triamine ligands, and mixed ligands.

2.3.2.1. Tripyridine ligands

Bulk ATRP promoted by CuX complexed by unsubstituted 2,2':6",2"-terpyridine (tpy) was heterogeneous for most monomers. Uncontrolled polymerizations were observed with molecular weight evolution resembling redox-initiated free radical polymerization. High molecular weight polymers were obtained within 0.5 h and polydispersities were close to 2 for the ATRP of styrene and MA. ATRP of styrene and MA promoted by CuX complexed by 4,4',4"-tris(5-nonyl)-2)2':6",2"-terpyridine (tNtpy) was initially homogeneous. As the polymerization proceeded, green precipitate formed. The polymerizations of styrene and MA were well controlled with molecular weights evolving linearly with conversion of monomers and polydispersities less than 1.2 [47]. The difference in the results between the polymerization using tpy and tNpy is attributed to the fact that tNtpy can better solublize copper complexes in nonpolar organic solvents and thus provide sufficient amount of the deactivating copper(II) species in the solution.

2.3.2.2. Triamine ligands

Tridentate linear amine, 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), has been used successfully as a ligand to promote ATRP under similar conditions as dNbpy [41]. In general, employment of multidentate aliphatic amines as ligands have the advantage of being commercially available and less expensive, causing less coloring to the polymerization solution and promoting a faster rate when compared with the bpy system. The polymerization media is heterogeneous for both styrene and MMA, but initially homogeneous for MA. With PMDETA as the ligand, the polymerization for styrene was faster than that using dNbpy, while the rate of polymerization of MA was comparable to that of copper/dNbpy. Linear semi-logarithmic kinetic plots were observed for both styrene and MA polymerizations; however, a severe curvature in kinetic plot was observed for MMA, suggesting the occurrence of a significant amount of termination reactions presumably due to a higher equilibrium constant. For all three monomers, molecular weight increased

linearly versus conversion. The polydispersity for styrene, MA and MMA were ca. 1.3,1.05 and 1.15, respectively.

Cyclic aliphatic amines, such as l,4,7-trimethyl-l,4,7-triazacyclononane (TMTACN) and l,5,9-trimethyl-l,5,9-triazacyclodeodecane (TMTACDD), were also used in ATRP. A similar spacer effect was observed as discussed previously in the case of bidentate ligands. Copper coordinated by a ligand with an ethylene linker (i.e., TMTACN) promoted well-controlled ATRP of styrene, MA and MMA. In contrast, copper coordinated by a ligand with a propylene linker (i.e., TMTACDD) yielded polymers with higher polydispersities under similar reaction conditions.

2.3.2.3. Tridentate ligands with mixed nitrogen types

There are many possible structures for tridentate ligands with mixed nitrogen types, and they can be formed by the combinations of any two of pyridine, imine, and amine or all three. The most studied is the combination of two pyridine and one amine, such as N,N-bis(2-pyridylmethyl)octylamine (BPMOA) which synthesized by the coupling of 2-picolyl chloride with n-octylamine (Figure 2.4.).

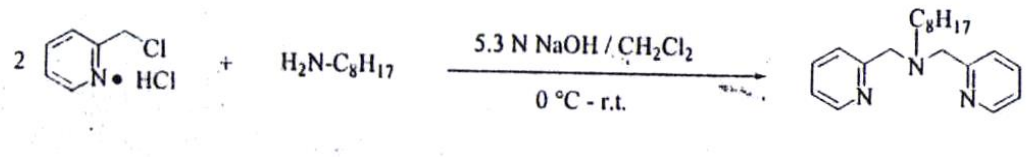


Figure 2.4 Synthesis of BPMOA

With BPMOA as the ligand, well-controlled polymerizations were carried out for styrene, MA and MMA. Polydispersities for all three monomers remained quite low (M_n/M_w < 1.2) [38]. Different from PMDETA, BPMOA yielded a linear kinetic plot for MMA, and this was attributed to the better solubility of the catalyst.

Other mixed nitrogen tridentate ligands containing a pyridine-imine moiety, such as N-(2-pyridylrnethyl)-(2-pyridyl)methanimine (PMPMI) and N-(2-N-(dimethyl)-ethyl)-(2-pyridyl)methanimine (DMEPMI) were synthesized by the condensation reactions using bidentate primary amines with 2-pyridinecarbox-aldehyde [46]. With PMPMI as the ligand, well-controlled polymerizations were obtained for both styrene and MA. However, less efficient control was observed for the polymerization

of MMA yielding polymers with polydispersities of 2.8. When DMEPMI was used as the ligand, well-controlled polymerizations were also obtained for both styrene and MA, and the control of MMA polymerization was slightly improved.

2.3.3. Tetradentate nitrogen ligands

For tetradentate ligands, ligand geometries other than linear or cyclic geometry are possible. Ligands with a tripodal structure have been found to form some of the most reactive catalytic systems in copper-mediated ATRP.

2.3.3.1. Tetramine ligands

Similarly to PMDETA, linear tetramine, 1,1,4,7,10,10-hexamethyltriethylene-tetramine (HMTETA) (Figure 2.8), has also been used successfully as the ligand to promote ATRP of Sty, MA and MMA [41]. In contrast to the copper/PMDETA system, a linear semi-logarithmic plot of conversion vs time was observed for MMA. Molecular weights increased linearly with conversion, and were close to the theoretical values for all three monomers. The polydispersities of the obtained polymers were very low ($M_n/M_w \sim 1.1$).

Copper complexed by a cyclic tetramine, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMTACTD, Figure 2.8), was found to afford polymers with much higher molecular weights than the predicted values and high polydispersities. High molecular weight polymers were obtained at relatively low monomer conversions, suggesting a slow deactivation process.

Controlled ATRP of acrylates can be carried out at ambient temperature using a tripodal tetramine, i.e., tris[2-(dimethylamino)ethyl]amine (Me6TREN) (Figure 2.5) [49]. The polymers obtained have molecular weights close to the theoretical values and narrow molecular weight distributions. The rate of polymerization was significantly faster than that with dNbpy or its linear counterpart. Conversion of 80% of MA was reached within 3 h at 22 °C with a catalyst to initiator to monomer ratio of 0.1/1/232. The polydispersities were as low as 1.09. It should be recognized that increased polymerization rate as a result of an increased radical concentration may adversely affect the polymerization control; however, this is less pronounced for

monomers with high rate constants of propagation, e.g., MA. The strong copper binding and fast rate of polymerization using Me_6TREN as the ligand was further applied to the controlled polymerization of 4-vinylpyridine [50].

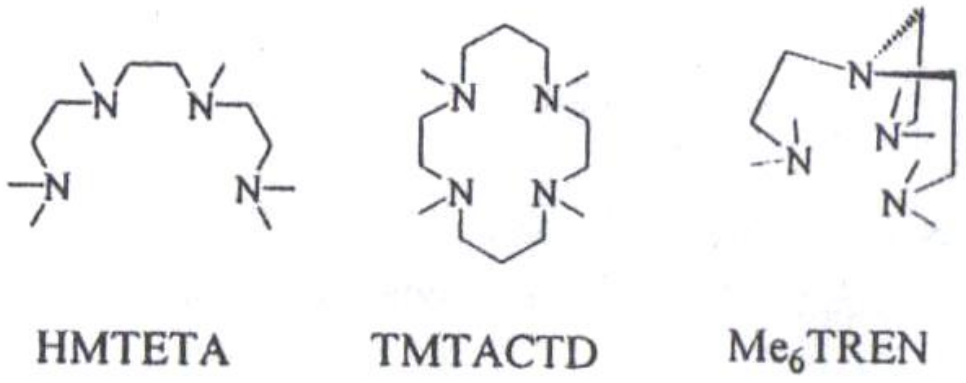


Figure 2.5 Linear, cyclic and branched (tripodal) tetradentate amine ligands

2.3.3.2. Tetradentate ligands with mixed nitrogen types

As in the case of tridentate mixed nitrogen ligands, there are many possible combinations and geometry possible. However, they have not been extensively studied so far. Two tetradentate ligands with mixed nitrogen types are shown in Figure 2.6.

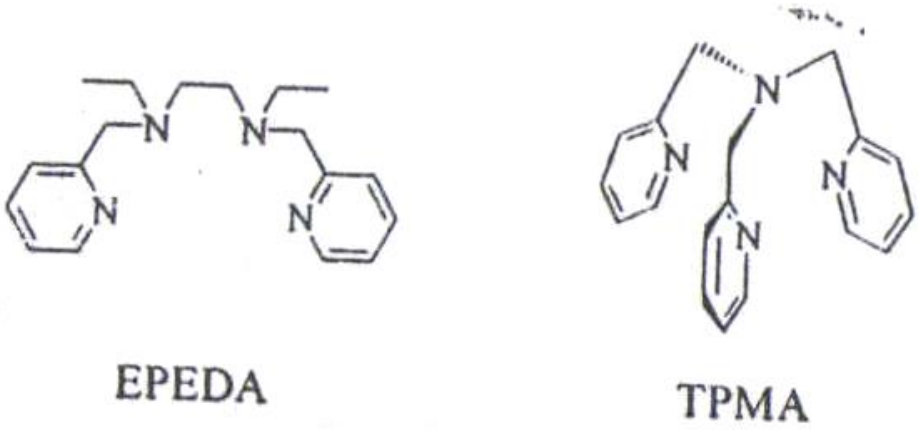


Figure 2.6 Two examples of tetradentate ligand with mixed nitrogen types

N,N'-diethyl-N,N'-bis[(2-pyridyl)methyl]ethylenediamine (EPEDA) and tris[(2-pyridyl)methyl]amine (TPMA) were synthesized by the coupling of two equivalents of 2-pycolylchloride with N,N'-diethyl-ethylenediamine and (2-aminomethyl) pyridine, respectively. Similar to its amine analog, Me_6TREN, TPMA as the ligand

promoted well-controlled polymerizations of Sty and MA at 110 °C and 50 °C, respectively [48]. For MA, a catalyst to initiator ratio of 0.2 was sufficient to produce well-defined polymers (M_n = 15200 and M_w/M_n = 1.05) within 1 h.

2.3.4. Linear amine ligands

The simple amines are of interest in ATRP for three general reasons. First, most of the simple amines are less expensive, more accessible and more tunable than 2,2'-bipyridine (bipy) ligands. Second, due to the absence of the extensive pi bonding in the simple amines, the subsequent copper complexes are less colored. Third, since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-bipy comples, the employment of simple amines as the ligand in ATRP may lead faster polymerization rates. Linear amine ligands with long alkyl substituents provide soluble ligand catalyst complexes in ATRP. In this thesis we especially focused on providing homogeneous polymerization medium by using alkyl substituted linear amine ligands that forms soluble complex with catalyst.

3. EXPERIMENTAL PART

3.1. Chemicals

Diethylenetriamine (DETA, 99%), triethylenetetramine (TETA, 60%), polyimine (Mw=423 g mol^{-1}), 1-bromopropane (98%), 1-bromobutane (99%), 1-bromopentane (98%), 1-bromohexane (98%), copper(I)bromide (CuBr, 99.99%) and potassium carbonate (99+%) were purchased from the Aldrich Chemical Co. MMA (99 %), S (99 %), bromoethane (98%), ethyl-2-bromoisobutyrate (E*i*BB, 98%), ethyl-2-bromopropionate (EBP, 99%) were purchased from Acros Organics Co. Ethanol (99.5%) and anhydrous sodium sulphate (99%) were purchased from J. T. Baker Co. All reagents were used without further purification.

3.2. Synthesis of Alkylated Linear Amine Ligands (ALALs)

Alkylated linear amin ligands (ALALs) that are derivatives of tridentate, tetradentate and multidentate linear amines; 1,1,4,7,7-pentaethyldiethylenetriamine (PEDETA), 1,1,4,7,7-pentapropyldiethylenetriamine (PPrDETA), 1,1,4,7,7-pentabutyldiethylene-triamine (PBDETA), 1,1,4,7,7-pentapentyldiethylenetriamine (PPeDETA), 1,1,4,7,7-pentahexyldiethylenetriamine (PHDETA), 1,1,4,7,10,10-hexaethyltriethylene-tetramine (HETETA), 1,1,4,7,10,10-hexapropyltriethylenetetramine (HPrTETA), 1,1,4,7,10,10-hexabutyltriethylenetetramine (HBTETA), 1,1,4,7,10,10-hexapentyl -triethylenetetramine (HPeTETA), 1,1,4,7,10,10-hexahexyltriethylenetetramine (HHTETA), and ethyl substituted polyimine (EPI) were synthesized according to a procedure described previously [1].

3.2.1. Synthesis of 1,1,4,7,7-pentaethyldiethylenetriamine (PEDETA)

Ethyl bromide (0.255 mol) solution in ethanol (100 ml) was added dropwise to DETA at 5 ^{o}C. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was stirred for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued stirring for 3 more days. Then ~300

ml of distilled water and 100 ml of ethyl acetate were added in order to separate the organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavaporator. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. PEDETA: ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.9-1.0 (m. 15 H), 2.44 (t. 18 H).

3.2.2. Synthesis of 1,1,4,7,7-pentapropyldiethylenetriamine (PPrDETA)

1-Bromo propane (0.255 mol) solution in ethanol (100 ml) was added dropwise to DETA at room temperature. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was refluxed for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued refluxing for 3 more days. Then ~300 ml of distilled water and 100 ml of ethyl acetate were added in order to separate the organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavaporator. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.66-0.68 (m. 15 H), 1.25-1.27 (m. 10 H), 2.3 (t. 18 H).

3.2.3. Synthesis of 1,1,4,7,7-pentabutyldiethylenetriamine (PBDETA)

1-Bromo butane (0.255 mol) solution in ethanol (100 ml) was added dropwise to DETA at room temperature. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was refluxed for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued refluxing for 3 more days. Then ~300 ml of distilled water and 100 ml of ethyl acetate were added in order to separate the organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavaporator. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.9-1.0 (m. 15 H), 1.30-1.34 (m. 20 H), 2.44 (t. 18 H).

3.2.4. Synthesis of 1,1,4,7,7-pentapentyldiethylenetriamine (PPeDETA)

1-Bromo pentane (0.255 mol) solution in ethanol (100 ml) was added dropwise to DETA at room temperature. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was refluxed for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued refluxing for 3 more days. Then ~300 ml of distilled water and 100 ml of ethyl acetate were added in order to separate the organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavaporator. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.9-1.0 (m. 15 H), 1.26-1.30 (m. 30 H), 2.44 (t. 18 H).

3.2.5. Synthesis of 1,1,4,7,7-pentahexyldiethylenetriamine (PHDETA)

1-Bromo hexane (0.255 mol) solution in ethanol (100 ml) was added dropwise to DETA at room temperature. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was refluxed for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued refluxing for 3 more days. Then ~300 ml of distilled water and 100 ml of ethyl acetate were added in order to separate the organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavaporator. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.7-0.9 (m. 15 H), 1.28-1.32 (m. 40 H), 2.45 (t. 18 H).

3.2.6. Synthesis of 1,1,4,7,10,10-hexaethyltriethylenetetramine (HETETA)

Ethyl bromide (0.305 mol) solution in ethanol (100 ml) was added dropwise to TETA at 5 ^{o}C. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was stirred at RT for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued stirred for 3 more days. Then ~300 ml of distilled water and 100 ml of ethyl acetate were added in order to separate the

organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavap. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.0-1.1 (m. 18 H), 2.45-2.55 (t. 24 H).

3.2.7. Synthesis of 1,1,4,7,10,10-hexapropyltriethylenetetramine (HPrTETA)

1-Bromo propane (0.305 mol) solution in ethanol (100 ml) was added dropwise to TETA at room temperature. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was refluxed for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued refluxing for 3 more days. Then ~300 ml of distilled water and 100 ml of ethyl acetate were added in order to separate the organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavap. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.9-1.0 (m. 18 H), 1.30-1.32 (m. 12 H), 2.4-2.5 (t. 24 H).

3.2.8. Synthesis of 1,1,4,7,10,10-hexabutyltriethylenetetramine (HBTETA)

1-Bromo butane (0.305 mol) solution in ethanol (100 ml) was added dropwise to TETA at room temperature. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was refluxed for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued refluxing for 3 more days. Then ~300 ml of distilled water and 100 ml of ethyl acetate were added in order to separate the organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavap. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.80-0.84 (m. 18 H), 1.26-1.30 (m. 24 H), 2.38 (t. 24 H).

3.2.9. Synthesis of 1,1,4,7,10,10-hexapentyltriethylenetetramine (HPeTETA)

1-Bromo pentane (0.305 mol) solution in ethanol (100 ml) was added dropwise to TETA at room temperature. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was refluxed for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued refluxing for 3 more days. Then ~300 ml of distilled water and 100 ml of ethyl acetate were added in order to separate the organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavap. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.82-0.84 (m. 18 H), 1.30-1.36 (m. 36 H), 2.40-2.45 (t. 24 H).

3.2.10. Synthesis of ethylated polyimine (EPI)

Ethyl bromide (1.1 mol) solution in ethanol (100 ml) was added dropwise to Polyimine (M_n = 423 g mole^{-1}) at 5 ^{o}C. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was stirred for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued sttiring for 3 more days. Then ~300 ml of distilled water and 100 ml of ethyl acetate were added in order to separate the organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavap. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.2 (m. 36 H), 2.48-2.50 (t. 60 H).

3.3. Investigation of ATRP Conditions for Alkylated Linear Amine Ligands

A typical ATRP procedure was performed as follows. Catalyst, Cu(I)Br was placed in a 48 ml of flask, which contained a side arm with a Teflon valve sealed with a Teflon stopper. Then the flask was deoxygenated by vacuum-traw-nitrogen circles. MMA (6.24 mol l^{-1}) or S (7.93 mol l^{-1}), anisole and ligand were added to the flask. Finally, an appropriate initiator (E*i*BB for MMA and EBP for S) was added then the flask was replaced in thermostatically controlled oil bath at given temperatures. All

liquid components were nitrogen bubbled prior to placement into the flask. Monomer/initiator/catalyst/ligand ratio was mentioned in Section 3.3.1, Section 3.3.2 and Section 3.3.3 according to the optimization parameters. Samples were taken periodically via a syringe to follow the kinetics of the polymerization process. The samples were diluted with THF and methanol was added. GC and GPC measurements were performed.

3.3.1. Ligand Ratio

Styrene, ethyl-2-bromopropionate, and CuBr were used as monomer, initiator and catalyst, respectively. PPrDETA was used as a ligand. Three different set was prepared with the ratios of ($[M]_o/[I]_o/[CuBr]_o/[L]_o$) 200/1/1/1, 200/1/1/2 and 200/1/1/3 in order to investigate the effect of the amount of ALALs in ATRP systems. The reaction temperatures are kept constant at 110 ^oC.

3.3.2. Catalyst Ratio

Styrene, ethyl-2-bromopropionate, and PPrDETA were used as monomer, initiator and ligand, respectively. CuBr was used as a catalyst. Three different set was prepared with the ratios of ($[M]_o/[I]_o/[CuBr]_o/[L]_o$) 200/1/1/3, 200/1/1,5/3 and 200/1/2/3 in order to investigate the effect of the amount of catalyst in ATRP systems. The reaction temperatures are kept constant at 110 ^oC.

3.3.3. Temperature Effect

Methyl methacrylate, ethyl-2-bromobutyrate, CuBr and PEDETA were used as monomer, initiator, catalyst and ligand, respectively. The ratio for all sets were kept constant as $[M]_o/[I]_o/[CuBr]_o/[L]_o$ = 200/1/1/1 . ($[M]_o/[I]_o/[CuBr]_o/[L]_o$) Three oil baths were set to 70 ^oC, 80 ^oC and 90 ^oC in order to investigate the effect of the temperature in ATRP systems.

3.4. Characterization

The ^1H NMR spectrum were recorded on a Bruker spectrometer (250 MHz for proton) in $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standart for the characterization of ALALs.

Monomer conversion was determined using an ATI Unicam 610 Series Gas Chromotograph equipped with a FID detector using a J&W Scientific 15 m DB WAX Widebore. Injector and detector temperatures were kept constant at 280 ^{o}C and 285 ^{o}C, respectively. Initial column temperature is 40 ^{o}C, finally reaching up to 120 ^{o}C with a heating rate of 40 ^{o}C / min.

Molecular weight and molecular weight distributions were determined by a gel permeation chromatography (GPC) instrument. An Agilent Model 1100 consisting of a pump, a refractive index detector and four Waters Styragel columns HR 5E, HR 4E, HR 3, HR 2; and THF was used as eluent at a flow rate of 0.3 ml/min at 30 ^{o}C. Molecular weights were calibrated using poly(methyl methacrylate) and polystyrene standards.

4. RESULTS AND DISCUSSIONS

4.1. Synthesis and characterization of ALALs

Alkylated linear amin ligands (ALALs) that are derivatives of tridentate, tetradentate and multidentate linear amines; 1,1,4,7,7-pentaethyldiethylenetriamine (PEDETA), 1,1,4,7,7-pentapropyldiethylenetriamine (PPrDETA), 1,1,4,7,7-pentabutyldiethylene-triamine (PBDETA), 1,1,4,7,7-pentapentyldiethylenetriamine (PPeDETA), 1,1,4,7,7-pentahexyldiethylenetriamine (PHDETA), 1,1,4,7,10,10-hexaethyltriethylene-tetramine (HETETA), 1,1,4,7,10,10-hexapropyltriethylenetetramine (HPrTETA), 1,1,4,7,10,10-hexabutyltriethylenetetramine (HBTETA), 1,1,4,7,10,10-hexapentyl -triethylenetetramine (HPeTETA), 1,1,4,7,10,10-hexahexyltriethylenetetramine (HHTETA), and ethyl substituted polyimine (EPI) were synthesized according to a procedure described previously.

The ^{1}H NMR spectra were recorded on a Bruker spectrometer (250 MHz for proton) in $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standard for the characterization of ALALs. The structures and purity of the ligands were assigned by the use of ^{1}H NMR spectra that are given below.

PEDETA has two different types of hydrogen atoms, which are attached to the adjacent carbon atom of the nitrogen (represented as “a”) and the others are attached to the end carbon atom of alkyl substituents (represented as “b”). The ratio of integral value of those hydrogen atoms was found identical with the theoretical ratio (18/15, a/b) as shown in Figure 4.1.

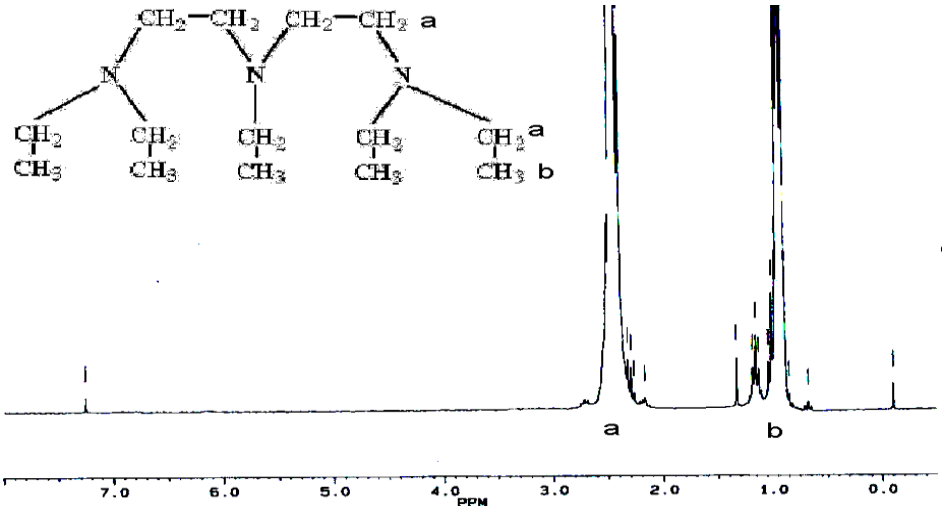


Figure 4.1 ^{1}H NMR spectrum of PEDETA in $CDCl_3$

PPrDETA has three different types of hydrogen atoms, which are attached to the adjacent carbon atoms of the nitrogen (represented as "a"), to the end carbon atom (represented as "b") and to the carbon atom between them (represented as "c"). The ratio of integral value of those hydrogen atoms was found identical with the theoretical ratio (18/15/10, a/b/c), as shown in Figure 4.2.

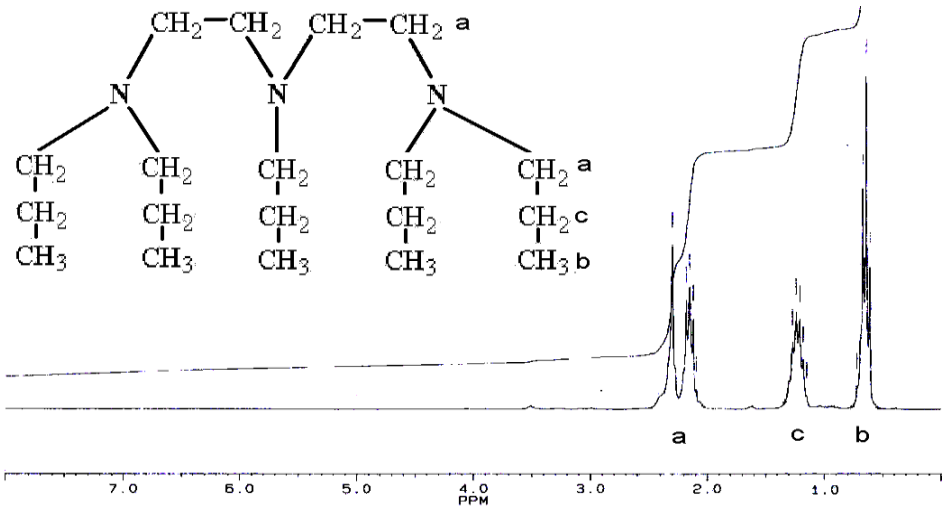


Figure 4.2 ^{1}H NMR spectrum of PPrDETA in $CDCl_3$

PBDETA has three different types of hydrogen atoms, which are attached to the adjacent carbon atom of the nitrogen (represented as "a"), to the end carbon atom (represented as "b") and to the carbon atom between them (represented as "c"). The ratio of integral value of those hydrogen atoms was found identical with the theoretical ratio (18/15/20, a/b/c), as shown in Figure 4.3.

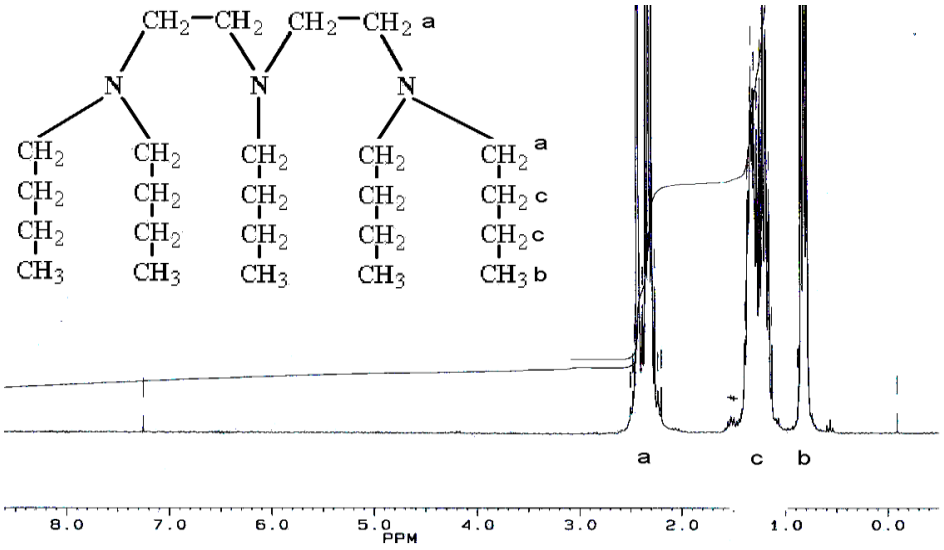


Figure 4.3 ^{1}H NMR spectrum of PBDETA in $CDCl_3$

PPeDETA has three different types of hydrogen atoms, which are attached to the adjacent carbon atom of the nitrogen (represented as "a"), to the end carbon atom (represented as "b") and to the carbon atom between them (represented as "c"). The ratio of integral value of those hydrogen atoms was found identical with the theoretical ratio (18/15/30, a/b/c), as shown in Figure 4.4.

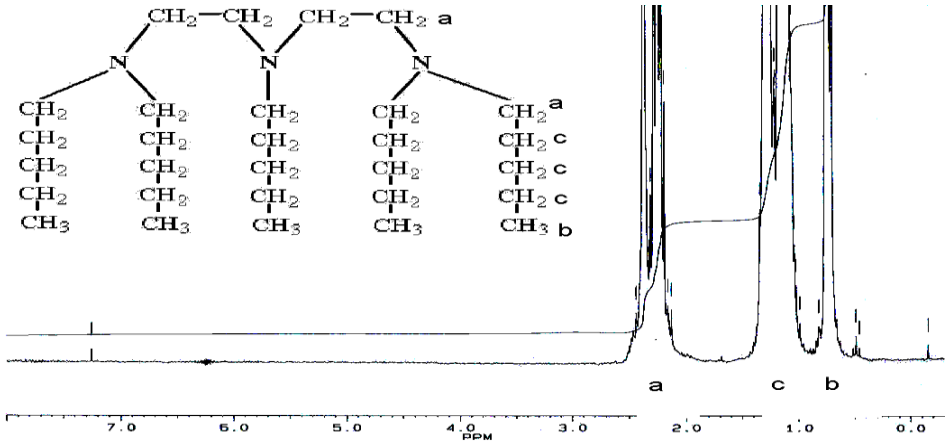


Figure 4.4 ^{1}H NMR spectrum of PPeDETA in $CDCl_3$

PHDETA has three different types of hydrogen atoms, which are attached to the adjacent carbon atom of the nitrogen (represented as "a"), to the end carbon atom (represented as "b") and to the carbon atom between them (represented as "c"). The ratio of integral value of those hydrogen atoms was found identical with the theoretical ratio (18/15/40, a/b/c), as shown in Figure 4.5.

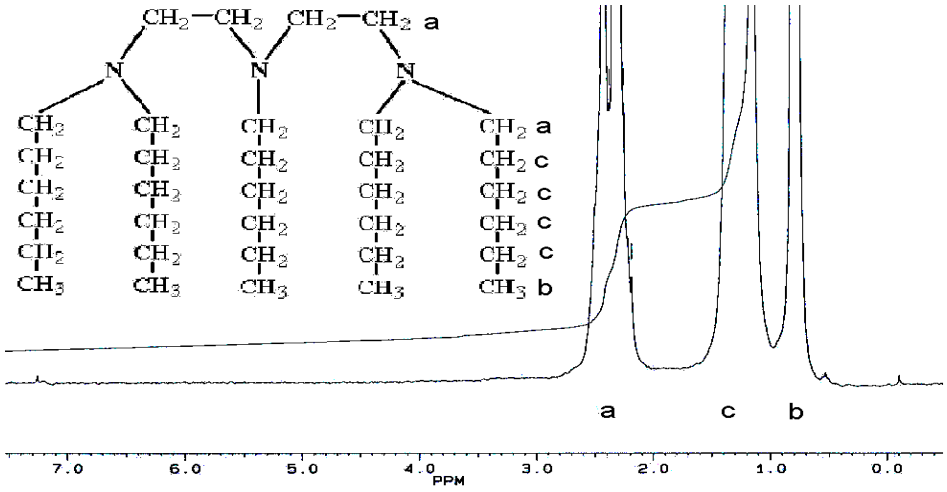


Figure 4.5 ^{1}H NMR spectrum of PHDETA in $CDCl_3$

HETETA has two different types of hydrogen atoms, which are attached to the adjacent carbon atom of the nitrogen (represented as "a") and the others are attached to the end carbon atom of alkyl substituents (represented as "b"). The ratio of integral value of those hydrogen atoms was found identical with the theoretical ratio (24/18, a/b) as shown in Figure 4.6.

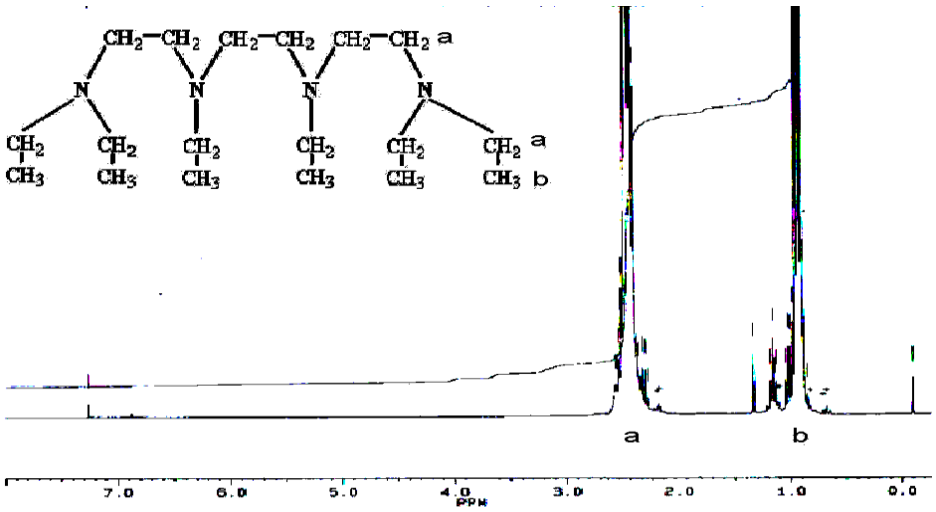


Figure 4.6 ^{1}H NMR spectrum of HETETA in $CDCl_3$

HPrTETA has three different types of hydrogen atoms, which are attached to the adjacent carbon atom of the nitrogen (represented as "a"), to the end carbon atom (represented as "b") and to the carbon atom between them (represented as "c"). The ratio of integral value of those hydrogen atoms was found identical with the theoretical ratio (24/18/12, a/b/c), as shown in Figure 4.7.

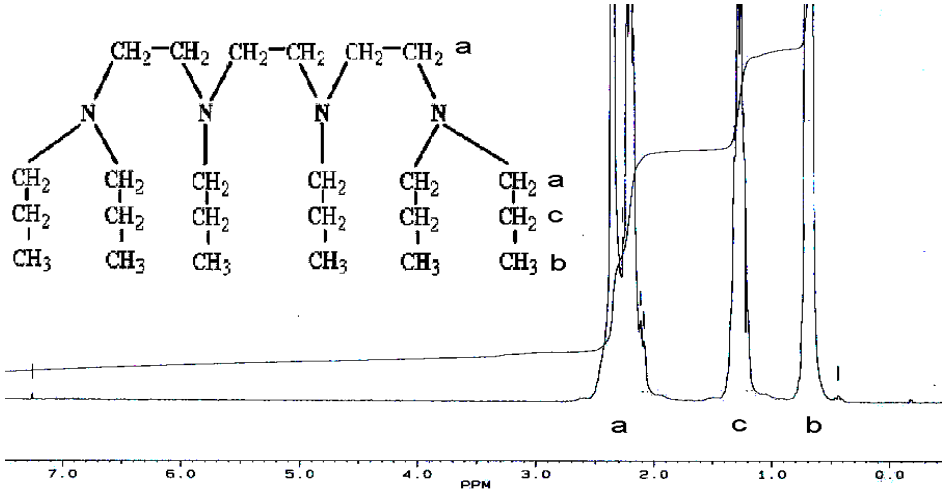


Figure 4.7 ^{1}H NMR spectrum of HPrTETA in $CDCl_3$

HBTETA has three different types of hydrogen atoms, which are attached to the adjacent carbon atom of the nitrogen (represented as "a"), to the end carbon atom (represented as "b") and to the carbon atom between them (represented as "c"). The ratio of integral value of those hydrogen atoms was found identical with the theoretical ratio (24/18/24, a/b/c), as shown in Figure 4.8.

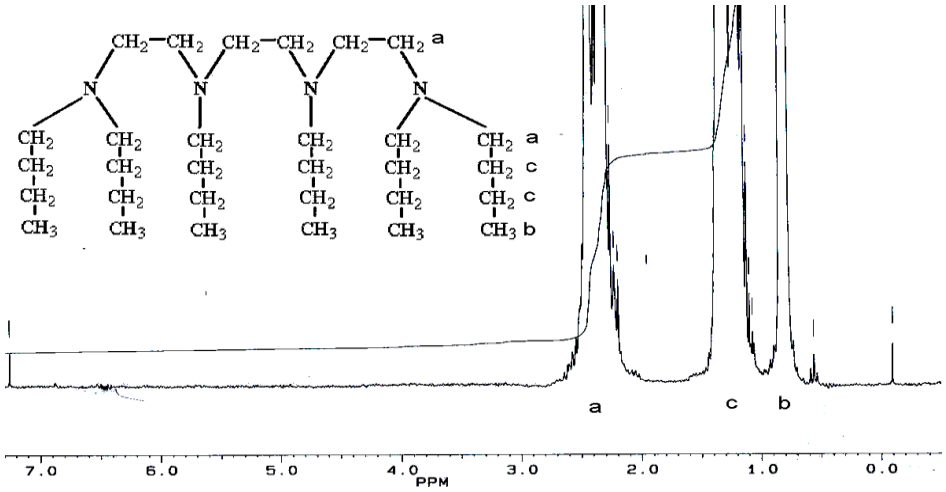


Figure 4.8 ^{1}H NMR spectrum of HBTETA in $CDCl_3$

HPeTETA has three different types of hydrogen atoms, which are attached to the adjacent carbon atom of the nitrogen (represented as "a"), to the end carbon atom (represented as "b") and to the carbon atom between them (represented as "c"). The ratio of integral value of those hydrogen atoms was found identical with the theoretical ratio (24/18/36, a/b/c), as shown in Figure 4.9.

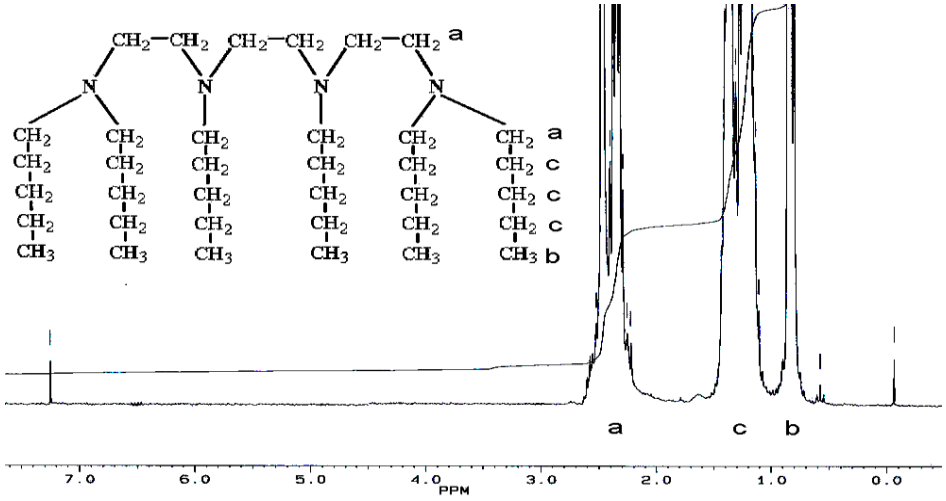


Figure 4.9 ^{1}H NMR spectrum of HPeTETA in $CDCl_3$

EPI has two different types of hydrogen atoms, which are attached to the adjacent carbon atom of the nitrogen (represented as "a") and the others are attached to the end carbon atom of alkyl substituents (represented as "b"). The ratio of integral value of those hydrogen atoms was found identical with the theoretical ratio (60/36, a/b) as shown in Figure 4.10.

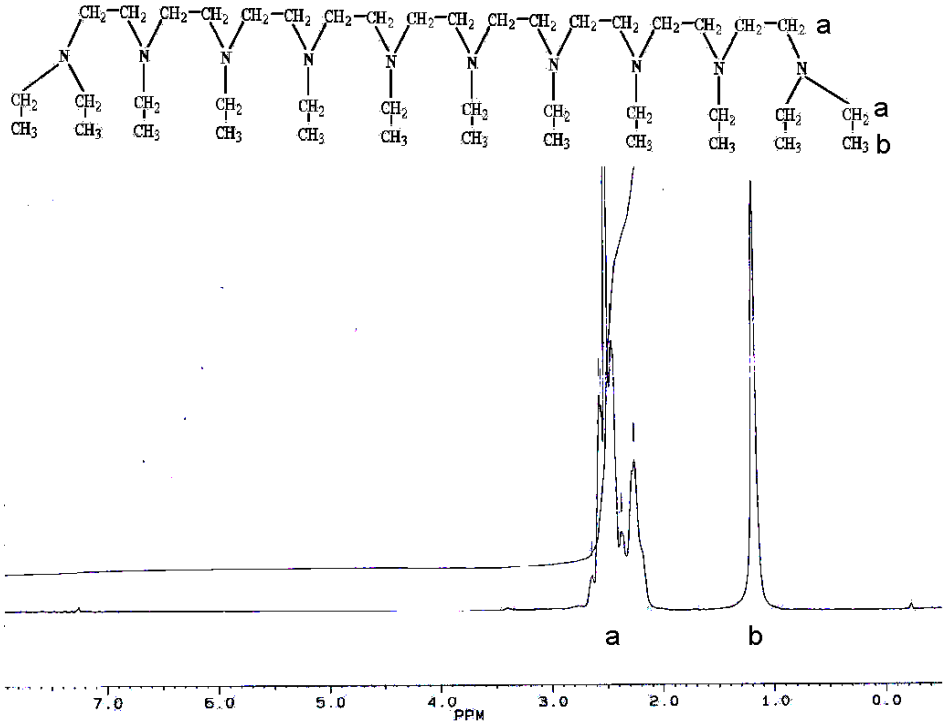


Figure 4.10 ^{1}H NMR spectrum of EPI in $CDCl_3$

4.2. Investigation of ATRP conditions for ALALs

A typical ATRP procedure was performed as explained in Section 3.3. The effects of ligand and catalyst ratio in ATRP of styrene were investigated. The effect of temperature in ATRP of methyl methacrylate was also investigated.

As mentioned in Section 2.3, concentration of the ligand is one of the most important parameter for ATRP. In order to explore this parameter, kinetic studies were performed with three different ratios that are 200/1/1/1, 200/1/1/2 and 200/1/1/3 for $[St]_o/[EBP]_o/[CuBr]_o/[PPrDETA]_o$. All reactions temperatures for ATRP of styrene were set up constant at 110 ^oC. The homogeneous reaction media was observed, which indicates the formation of soluble ligand-catalyst complex in organic solvents. According to the kinetic plots in Figure 4.11 the increase in ligands concentration provides fast polymerization rate. Apparent rates of styrene polymerization with the ratios of 200/1/1/1, 200/1/1/2 and 200/1/1/3 were found $0.88 \times 10^{-4}\ s^{-1}$, $1.12 \times 10^{-4}\ s^{-1}$ and $1.40 \times 10^{-4}\ s^{-1}$, respectively. The molecular weights and molecular weight distributions of styrene polymerization (last point of kinetic data) was measured by GPC as 15 100 g $mole^{-1}$, 20 300 g $mole^{-1}$ and 23 100 g $mole^{-1}$, 1.25, 1.18 and 1.25, respectively.

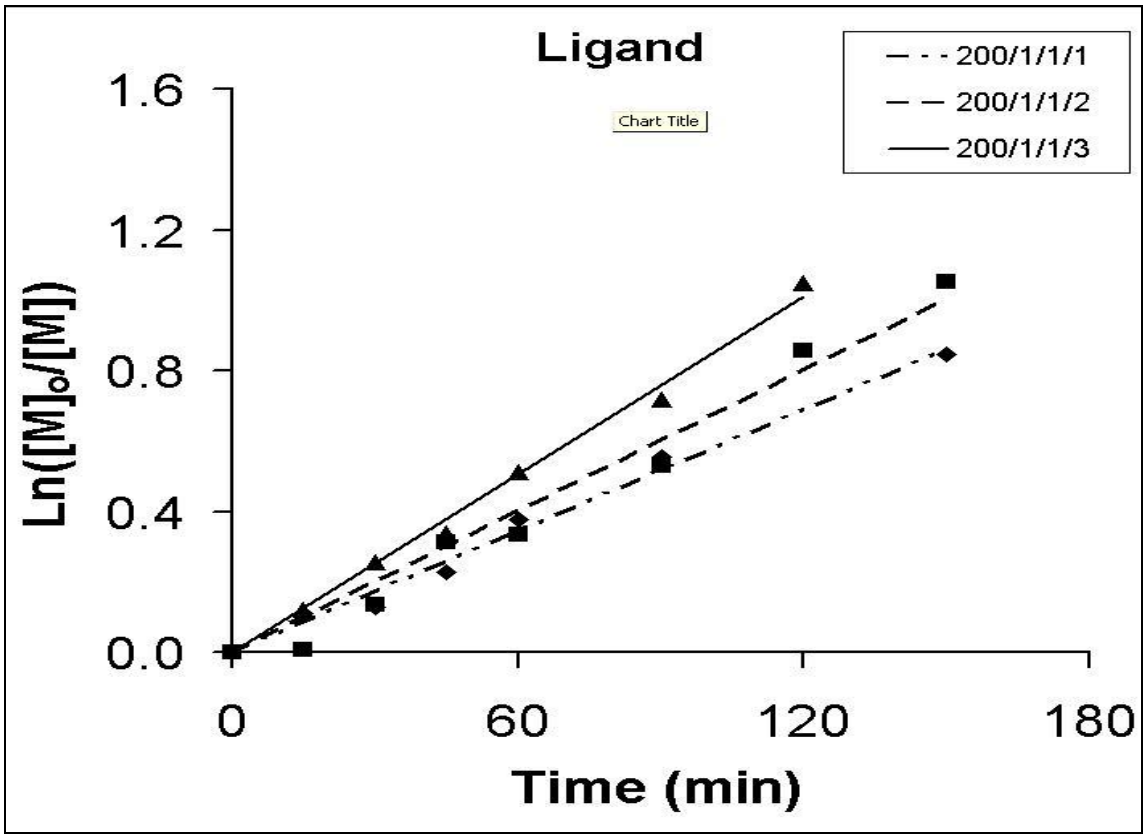


Figure 4.11 Kinetic plot of Styrene (110 ^{o}C) polymerizations. [S]: 7.93 mol l^{-1} in anisole; [EBP]:[CuBr] = 3.96.x 10^{-2} mol l^{-1}; ▲, [PPrDETA] = 1.19 x 10^{-1} mol l^{-1}; ■, [PPrDETA] = 7.93 x 10^{-1} mol l^{-1}; ♦, [PPrDETA] = 3.96 x 10^{-2} mol l^{-1}.

Concentration of the catalyst is another important parameter in ATRP systems. In order to investigate the effect of catalyst concentration, kinetic studies were performed with three different ratios that are 200/1/1/3, 200/1/1.5/3 and 200/1/2/3 for $[St]_o/[EBP]_o/[CuBr]_o/[PPrDETA]_o$. All reaction temperatures for ATRP of styrene were set up constant at 110 ^{o}C. The homogeneous reaction media was observed, which indicates the formation of soluble ligand-catalyst complex in organic solvents. According to the kinetic plots in Figure 4.11, the decrease in concentration of catalyst provides faster polymerization rate. Apparent rates of styrene polymerization with the ratios of 200/1/1/3, 200/1/1.5/3 and 200/1/2/3 were found 1.40 x 10^{-4} s^{-1}, 1.22 x 10^{-4} s^{-1} and 1.20 x 10^{-4} s^{-1}, respectively. The molecular weights and molecular weight distributions of styrene polymerization (last point of kinetic data) was measured by GPC as 23 100 g $mole^{-1}$, 20 900 g $mole^{-1}$ and 22 900 g $mole^{-1}$, 1.25, 1.23 and 1.23, respectively.

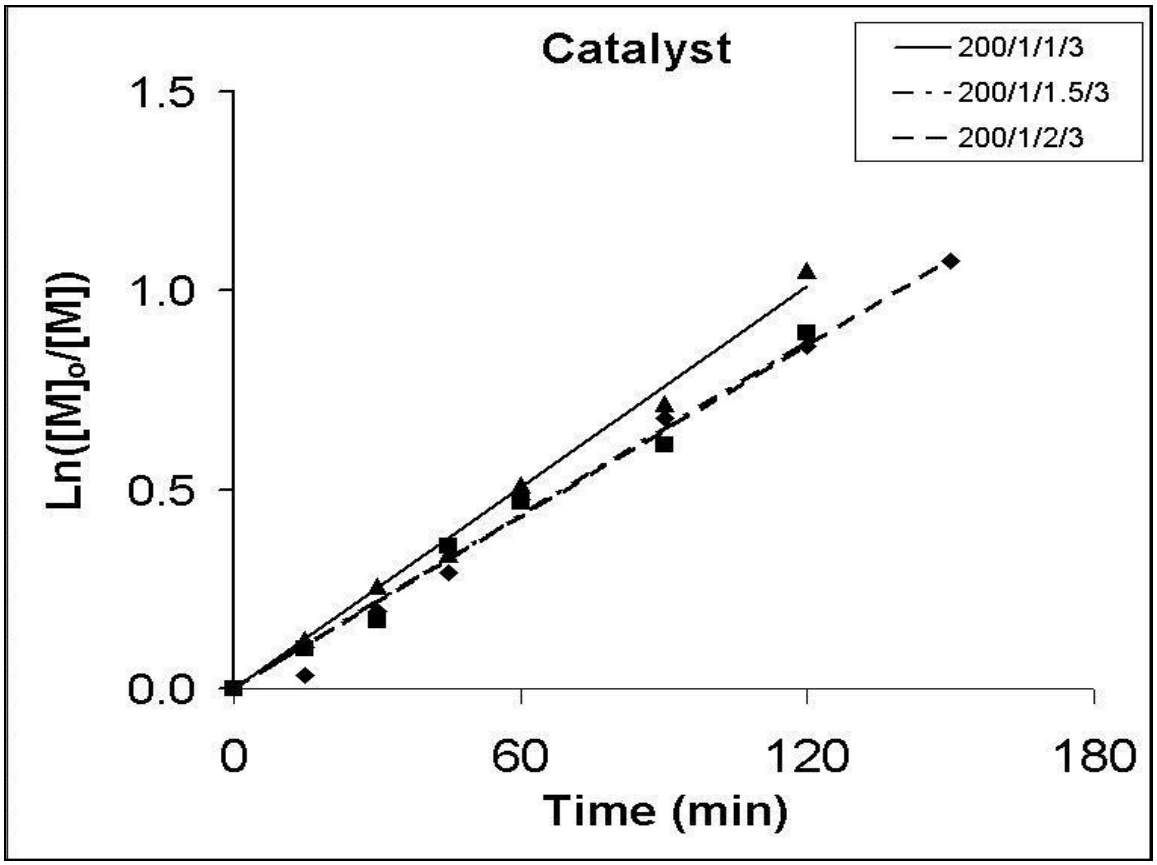


Figure 4.12 Kinetic plot of Styrene (110 ^{o}C) polymerizations. [S]: 7.93 mol l^{-1} in anisole; [EBP]: 3.96.x 10^{-2} mol l^{-1}; [PPrDETA]: 1.19 x 10^{-1} mol l^{-1}; ▲, [CuBr] = 3.96 x 10^{-2} mol l^{-1}; ■, [CuBr] = 5.94 x 10^{-2} mol l^{-1}; ♦, [CuBr] = 7.93 x 10^{-2} mol l^{-1}.

The temperature of the reaction is directly proportional with the polymerization rate of methyl methacrylate. In order to examine the effect of reaction temperature, kinetic studies were performed in three different temperatures that are 70 ^{o}C, 80 ^{o}C and 90 ^{o}C. The ratio of $[MMA]_o/[E\mathit{i}BB]_o/[CuBr]_o/[PEDETA]_o$ was kept constant as 200/1/1/1 and anisole (100 vol%) used as a solvent. The homogeneous reaction media was observed, which indicates the formation of soluble ligand-catalyst complex in organic solvents. According to the semi-logarithmic kinetic plot for ATRP of methyl methacrylate at different temperatures, the increase in reaction temperatures provides faster polymerization rate. Apparent rates of methyl methacrylate polymerization with the temperatures of 70 ^{o}C, 80 ^{o}C and 90 ^{o}C were found 0.85 x 10^{-4} s^{-1}, 1.75 x 10^{-4} s^{-1}, respectively. The molecular weights and molecular weight distributions of methyl methacrylate polymerization (last point of kinetic data) was measured by GPC as and 2.47 x 10^{-4} s^{-1}, 16 700 g $mole^{-1}$, 21 300 g $mole^{-1}$ and 21 000 g $mole^{-1}$, 1.13, 1.17 and 1.22, respectively.

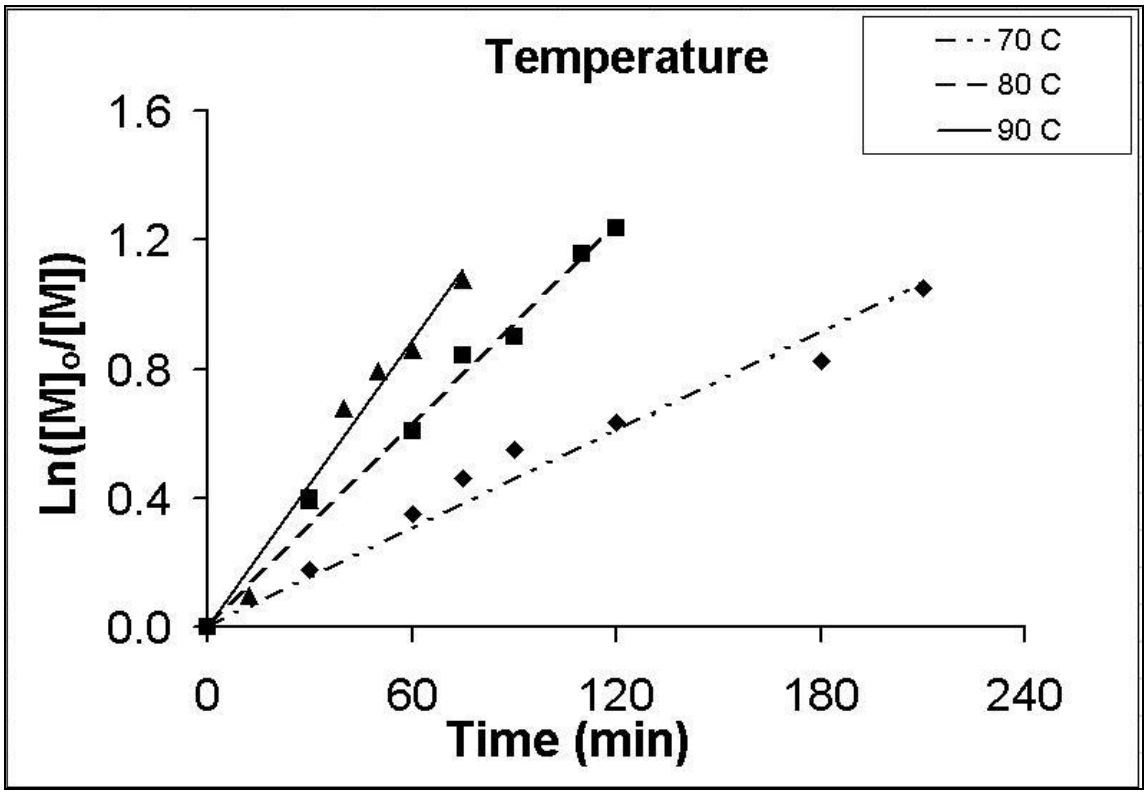


Figure 4.13 Kinetic plot of Methyl methacrylate polymerizations. [MMA]: 4.68 mol l^{-1} in anisole; [MMA]: [E*i*BB]: [CuBr]: [PPrDETA] = 200: 1: 1: 1; ▲, 90 ^{o}C; ■, 80 ^{o}C; ♦, 70 ^{o}C.

5. CONCLUSION

In this study, alkylated linear amin ligands (ALAL) that are derivatives of tridentate, tetradentate and multidentate linear amines; 1,1,4,7,7-pentaethyldiethylenetriamine (PEDETA), 1,1,4,7,7-pentapropyldiethylenetriamine (PPrDETA), 1,1,4,7,7-pentabutyldiethylenetriamine (PBDETA), 1,1,4,7,7-pentapentyldiethylenetriamine (PPeDETA), 1,1,4,7,7-pentahexyldiethylenetriamine (PHDETA), 1,1,4,7,10,10-hexaethyltriethylenetetramine (HETETA), 1,1,4,7,10,10-hexapropyltriethylenetetramine (HPrTETA), 1,1,4,7,10,10- hexabutyltriethylenetetramine (HBTETA), 1,1,4,7,10,10-hexapentyltriethylenetetramine (HPeTETA), 1,1,4,7,10,10-hexahexyl triethylenetetramine (HHTETA), and ethyl substituted polyimine (EPI) were synthesized by a simple and versatile reaction. All of ALALs were characterized by ^{1}H-NMR and gas chromatography.

Homogeneous reaction medium was observed during polymerization reactions of both styrene and methyl methacrylate, may due to soluble ALAL catalyst complex formation. The ATRP by using ALALs performed under homogeneous conditions and relatively fast polymerization rates were attained. Systematic investigation reviled that by changing methyl group of PMDETA to ethyl introduces homogeneity to the polymerization system.

The simple synthesis of a new class of ligands, alkylated linear amine ligands, ALALs, was demonstrated. The investigation of their effect on ATRP might contribute an attraction in polymer research groups by providing homogenous polymerization reaction medium and relatively fast polymerization rates with well-defined polymers.

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